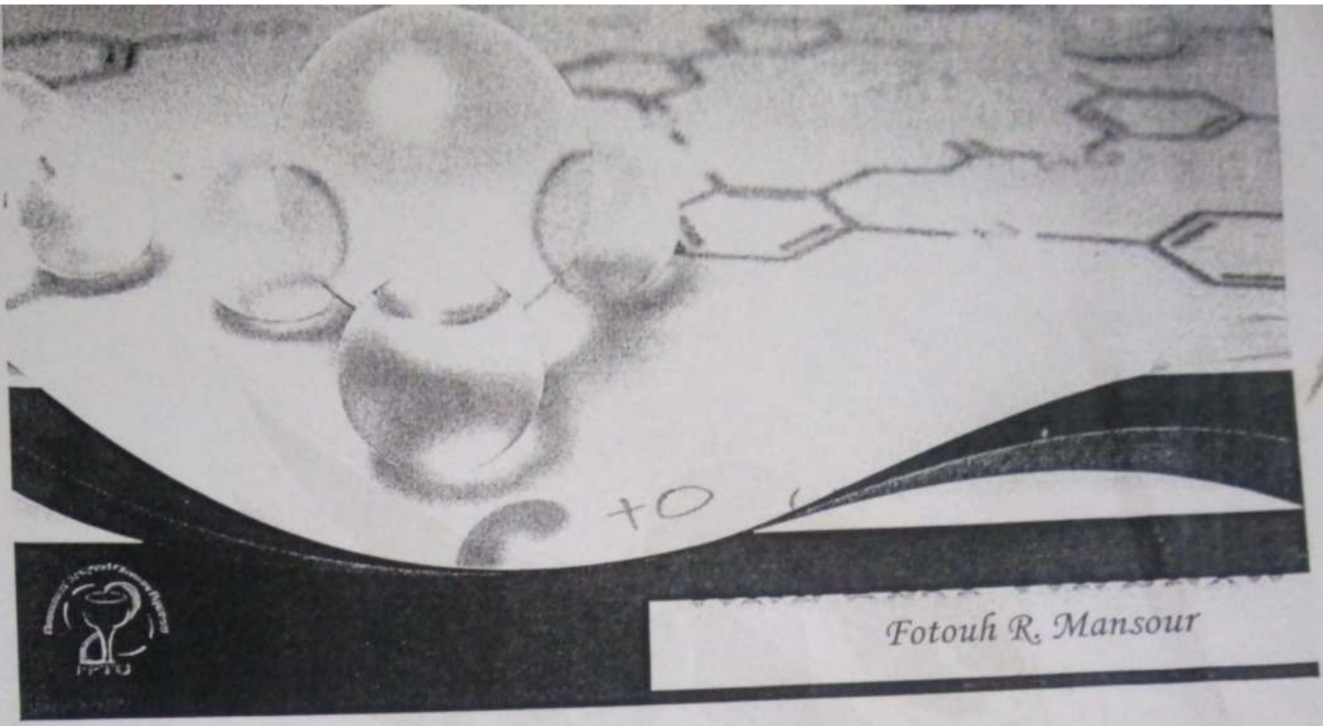


Fotouh R. Mansour

In this lecture:

Definitions of acids and bases

Strong & weak acids and bases

Salts

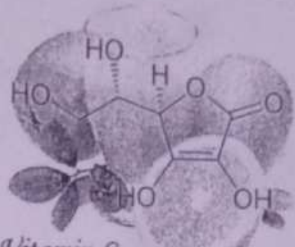
Equlibrium & ionic product of water

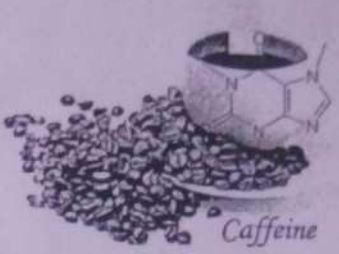
Ionization constant (Ka)

pH Scale

Acids and bases

- ✓ According to the taste
  - acid: sour
  - base: bitter
- ✓ Litmus paper
  - acid: red
  - base: blue


Vitamin C


Caffeine

Acids and bases

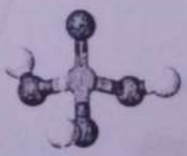
- ✓ According to the taste
  - acid: sour
  - base: bitter
- ✓ Litmus paper
  - acid: red
  - base: blue
- ✓ Antoine Lavoisier:
  - acid: oxygen-containing molecules
    - HCl? Does not have oxygen
    - bases? Not defined

H_2SO_4

H_2CO_3

HCl

HNO_3


H_3PO_4

Acids and bases

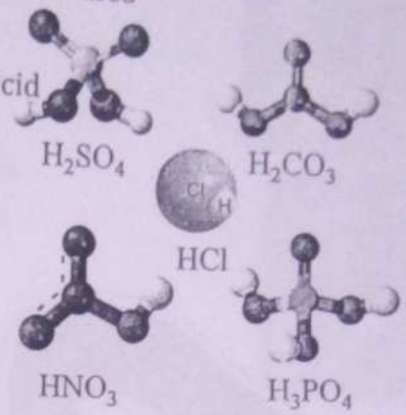
✓ Justus Liebig

acid: hydrogen-containing molecules

CH_4? Not an acid

HCl gas? Not a typical acid

bases? Not defined



CH_4

Acids and bases

✓ Justus Liebig

acid: hydrogen-containing molecules

CH_4? Not an acid

HCl gas? Not a typical acid

bases? Not defined

✓ Arrhenius ionization theory

acid: proton donor in water

base: hydroxyl ion donor in water

water is amphoteric

the solvent role? Not clear

H+? too small, does not exist alone

NH3 is a base? No OH^-

Acids and bases

- ✓ Brønsted–Lowry definition

  acid: proton donor

  base: proton acceptor

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

$$\underset{B}{NH_3} + \underset{A}{H_2O} \rightleftharpoons \underset{CA}{NH_4^+} + \underset{CB}{{}^-OH}$$

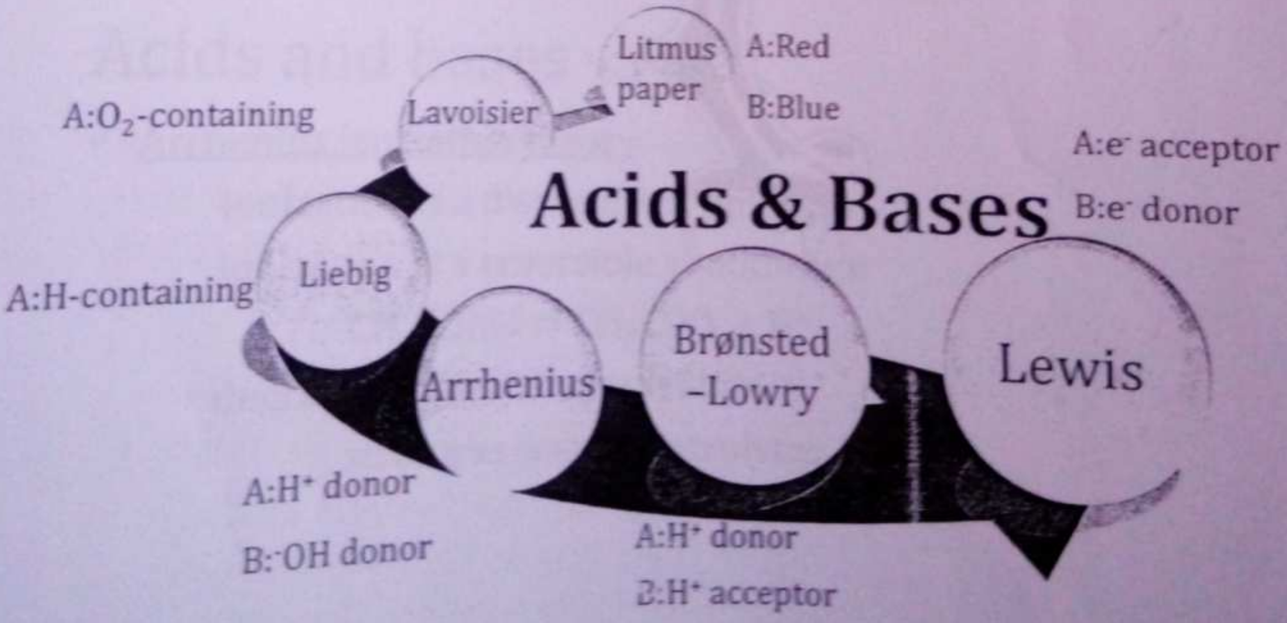
  Limitations:

  acids with no H^+ (e.g. BCl_3)

- ✓ Lewis definition

  acid: electron acceptor

  base: electron donor



Acids & Bases

Lavoisier

A:O_2-containing

Litmus paper

A:Red

B:Blue

Liebig

A:H-containing

Arrhenius

A:H^+ donor

B:^-OH donor

Brønsted –Lowry

A:H^+ donor

B:H^+ acceptor

Lewis

A:e^- acceptor

B:e^- donor

Acids and bases

- ✓ Arrhenius ionization theory

ionization is a dissociation process

$HCl \rightarrow H^+ + Cl^-$

$NaOH \rightarrow Na^+ + OH^-$

$NaCl \rightarrow Na^+ + Cl^-$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$H_2O \rightleftharpoons H^+ + OH^-$

$2H_2O \rightleftharpoons H_3O^+ + OH^-$

Acids and bases

- ✓ Arrhenius ionization theory

ionization is a dissociation process

ionization is a reversible equilibrium

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

degree of ionization is variant

strong vs weak electrolytes

Strong & weak acids and bases

- ✓ Strong acids & bases:
  - completely ionized
  - strong acids: HCl, HBr, HI, HNO_3, $HClO_4$, H_2SO_4
  - strong bases: hydroxides of gp I, $Ba(OH)_2$, $Ca(OH)_2$, and $Sr(OH)_2$
- ✓ Weak acids & bases:
  - partially ionized
  - weak acids: others
  - weak bases: others
  - Use double arrow (⇌) to indicate incomplete reaction

Acids, bases and Salts

- ✓ Salt: ionic compound containing an anion from an acid and a cation from a base
- ✓ For example: NaCl

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{NaOH} \rightarrow \underset{\text{salt}}{NaCl} + \underset{\text{water}}{H_2O}$$

- ✓ Types of salts:
  - Salt of strong acid and strong base NaCl
  - Salt of strong acid and weak base NH_4Cl
  - Salt of weak acid and strong base $NaCH_3COO$
  - Salt of weak acid and weak base NH_4CH_3Coo

Acids and bases

- ✓ Acid:
  1. has sour taste
  2. turns blue litmus paper red
  3. donates proton to form a conjugate base
  4. accepts electrons from bases
  5. reacts with bases to form salt and water
- ✓ Base:
  1. has bitter taste
  2. turns red litmus paper blue
  3. accepts proton to form a conjugate acid
  4. donates electrons to acids
  5. reacts with acids to form salt and water

Equilibrium

$$H_2O \rightleftharpoons H^+ + OH^-$$

- ✓ What is equilibrium?

  Forward rate = backward rate

- ✓ Constant concentrations

$$K_{eq} = \frac{[H^+][^-OH]}{[H_2O]}$$

- ✓ But $[H_2O]$ in dilute solutions is constant

$$K_w = [H^+][^-OH]$$

$$K_w = 1.0 \times 10^{-14}$$

(V)

Equilibrium

$H_2O \rightleftharpoons H^+ + OH^-$

$[H^+] = [OH^-]$

Equilibrium

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_w = [H^+][^-OH]$$

$$K_w = 1.0 \times 10^{-14}$$

- ✓ In pure water, $[H^+]=[^-OH]$

so, $K_w=[H^+]^2$

$1.0 \times 10^{-14}=[H^+]^2$

$[H^+] = 1.0 \times 10^{-7}$

$[^-OH] = 1.0 \times 10^{-7}$

Equilibrium

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_w = [H^+][^-OH]$$

- ✓ In neutral media, $[H^+] = [^-OH] = 1.0 \times 10^{-7}$
- ✓ In acidic media,

  $[H^+] > [^-OH]$

  $[H^+] > 1.0 \times 10^{-7}$

  The higher the $[H^+]$, the higher the acidic strength
- ✓ In basic media,

  $[^-OH] > [H^+]$

  $[^-OH] > 1.0 \times 10^{-7}$

Equilibrium

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

- ✓ What is equilibrium

  Forward rate = backward rate
- ✓ Constant concentrations

$$K = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

- ✓ Compare different acids
- ✓ Determine reaction feasibility

  reaction goes from stronger to weaker acids

Acid	Formula	K_a
Hydrochloric acid	HCl	>>1
Chlorous acid	$HClO_2$	1.1×10^{-2}
Nitrous acid	HNO_2	4.6×10^{-4}
Hydrofluoric acid	HF	3.5×10^{-4}
Hypochlorous acid	$HClO$	2.9×10^{-8}
Hydrocyanic acid	HCN	4.9×10^{-10}

Equilibrium

$^{-}CH_3 + \underset{SA}{\underline{NH_3}} \rightarrow \underset{WA}{\underline{CH_4}} + {}^{-}NH_2$ √

$^{-}OH + \underset{WA}{\underline{CH_4}} \rightarrow \underset{SA}{\underline{H_2O}} + {}^{-}CH_3$ X

$Cl^{-} + \underset{WA}{\underline{H_2O}} \rightarrow \underset{SA}{\underline{HCl}} + {}^{-}OH$ X

$^{-}NH_2 + \underset{SA}{\underline{H_2O}} \rightarrow \underset{WA}{\underline{NH_3}} + {}^{-}OH$ √

Stronger acid

Weaker base

Substance	Ka	CB
HCl	1.30×10^{6}	Cl^{-}
H_2O	1.99×10^{-16}	^{-}OH
NH_3	1.00×10^{-38}	$^{-}NH_2$
CH_4	1.00×10^{-50}	$^{-}CH_3$

Weaker acid

Stronger base

pH Scale

- ✓ $[H^+]$ in blood = $\frac{39}{1000000000} = 3.9 \times 10^{-8}$
- ✓ Søren Sørensen developed the pH scale in 1909
- ✓ $pH = -\log[H^+]$
- ✓ pH of blood = $-\log 3.9 \times 10^{-8} = 7.4$
- ✓ If $[H^+] = 1.0 \times 10^{-5}$

  $pH = -\log 1.0 \times 10^{-5} = 5.0$
- ✓ If $[H^+] = 7.4 \times 10^{-9}$

  $pH = -\log 7.4 \times 10^{-9} = 8.13$
- ✓ The lower the pH, the higher the acidity

pH Scale

- ✓ In neutral media, $[H^+]=[^-OH] = 1.0 \times 10^{-7}$

  $pH=-\log 1.0 \times 10^{-7}$

  $= 7$

  $pOH=-\log 1.0 \times 10^{-7}$

  $= 7$
- ✓ In acidic media, $pH<7$
- ✓ In basic media, $pH>7$
- ✓ $[H^+][^-OH]=K_w=10^{-14}$

  $pH + pOH = 14$

pH calculations

1. pH of strong acids

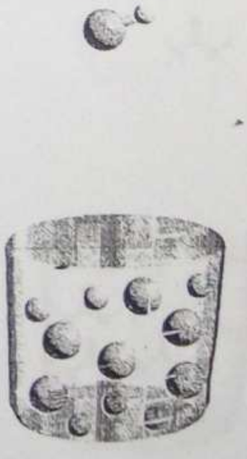
   e.g. HCl

   $HCl \rightarrow H^+ + Cl^-$

   $[H^+]=HCl$

   $= Ca$

   $pH=pCa$



What is the pH of a solution of 0.001 M HCl?

$pH=pCa=-\log 0.001=3$

pH calculations

2. pH of strong bases

e.g. NaOH

$NaOH \rightarrow Na^+ + {}^-OH$

$[{}^-OH] = NaOH$

$= C_b$

$pOH = pC_b$

What is the pH of a solution of 0.001 M NaOH?

$pOH = pC_b = -\log 0.001 = 3$

$pH = 14 - pOH = 14 - 3 = 11$

---

pH calculations

3. pH of weak acids

e.g. CH_3COOH $\quad CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

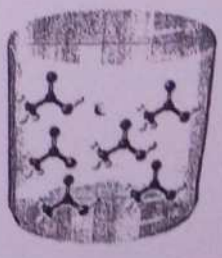
$[H^+] = [CH_3COOH]$? X

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

But $[H^+] = [CH_3COO^-]$

$$K_a = \frac{[H^+]^2}{[CH_3COOH]}$$

But $[CH_3COOH] = Ca$



$$K_a = \frac{[H^+]^2}{Ca}$$

$[H^+]^2 = Ka.Ca$

$[H^+] = (Ka.Ca)^{½}$

$pH = ½(pKa + pCa)$

pH calculations

4. pH of weak bases

e.g. NH_4OH $\qquad$ $NH_4OH \rightleftharpoons NH_4^+ + {}^-OH$

$[{}^-OH]=[NH_4OH]$? $\qquad$ X

$$K_b = \frac{[NH_4^+][{}^-OH]}{[NH_4OH]} \qquad \text{But } [{}^-OH] = [NH_4^+]$$

$$K_b = \frac{[{}^-OH]^2}{[NH_4OH]} \qquad \text{But } [NH_4OH] = C_b$$

$$K_b = \frac{[{}^-OH]^2}{C_b}$$

$$[{}^-OH]^2 = K_b . C_b$$

$$[{}^-OH] = (K_b . C_b)^{1/2}$$

$$pOH = \tfrac{1}{2}(pK_b + pC_b)$$

---

pH calculations

5. pH of salts of strong acid and strong base

e.g. NaCl $\qquad$ pH=7

6. pH of salts of strong acid and weak base

e.g. NH_4Cl

$$pH = \tfrac{1}{2}(pK_w - pK_b + pC_s)$$

7. pH of salts of strong base and weak acid

e.g. CH_3COONa

$$pH = \tfrac{1}{2}(pK_w + pK_a - pC_s)$$

8. pH of salts of weak acid and weak base

e.g. CH_3COONH_4

$$pH = \tfrac{1}{2}(pK_w + pK_a - pK_b)$$

pH calculations

Substance	The rule	The pH
SA	$pH = -\log C_a$	
SB	$pOH = -\log C_b$	$pH = 14 - pOH$
WA	$pH = ½(pka+pCa)$	
WB	$pOH = ½(pk_b+pC_b)$	$pH = 14 - pOH$
Salt of SA & SB	$pH = pOH = 7$	
Salt of SA & WB	$pH = ½(pK_w-pK_b+pC_s)$	
Salt of WA & SB	$pH = ½(pK_w+pK_a-pC_s)$	
Salt of WA & WB	$pH = ½(pK_w+pK_a-pK_b)$	

Acid Base Titration

Fotouh R. Mansour
February17th, 2015

This Lecture

✓ pH Scale & pH calculations

pH buffer systems

Titration & titration reactions

Titration curves

Color indicators

pH Buffer systems

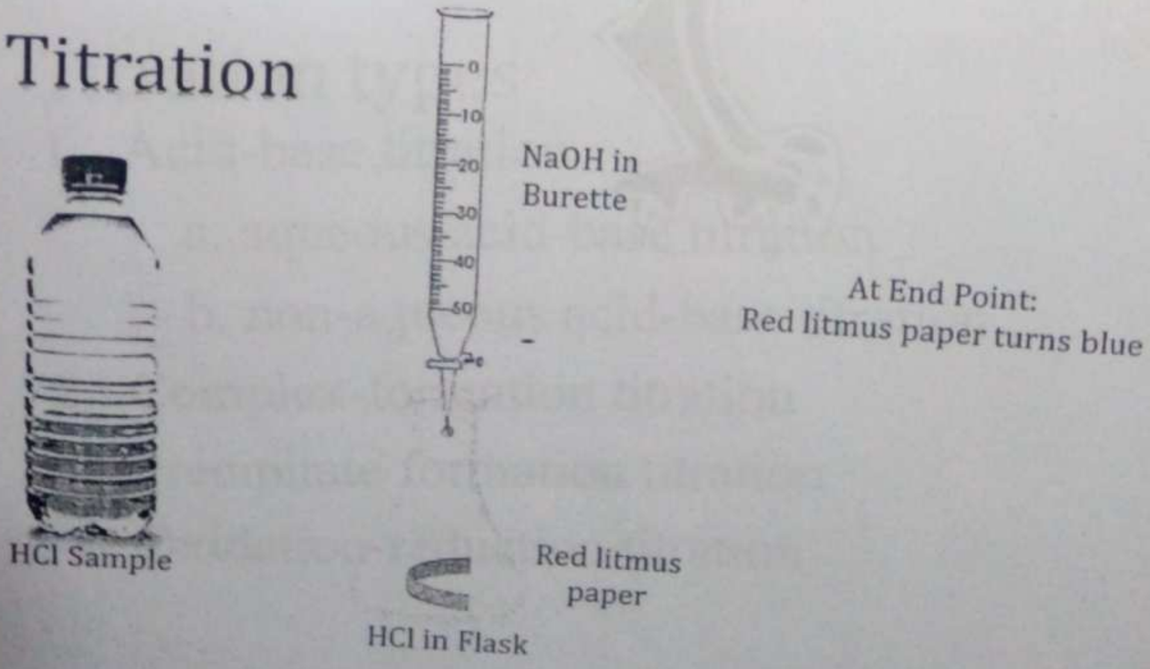
✓ pH buffer capacity

- a measure of the buffer ability to resist changes in the pH upon addition of small amounts of strong acid or base

$$\beta_{(b)} = \frac{dc_b}{dpH} \qquad \beta_{(a)} = -\frac{dc_a}{dpH}$$

- the amount of strong acid or strong base required to change the buffer pH by one unit
- to increase buffer capacity:
  1. use high concentrations
  2. use ratio close to one

Titration



Titration

- ✓ Titration: form of volumetric analysis in which increments of reagent solution—the titrant—are added to analyte until their reaction is complete.
- ✓ standard solution : A solution of accurately known concentration
- ✓ Sample: a portion selected from a larger quantity of material
- ✓ Analyte: The component of a system to be analysed.
- ✓ End point: the volume at which a change in the indicator visual property is observed.
- ✓ The equivalence point is the volume at which an added titrant and the analyte are stoichiometrically equal

Titration types

1. Acid-base titration
    a. aqueous acid-base titration
    b. non-aqueous acid-base titration
2. Complex-formation titration
3. Precipitate formation titration
4. Oxidation-reduction titration

Requirements of titration reaction

1. Single = no side reactions
2. Rapid

Oxidation of oxalate by permanganate

Add manganese (II) as a catalyst

Requirements of titration reaction

1. Single = no side reactions
2. Rapid
3. Stoichiometric

Methylation of benzene is non-stoichiometric

$C_6H_6 + CH_3Cl \rightarrow C_6H_5CH_3 + HCl$

$C_6H_6 + 2\ CH_3Cl \rightarrow C_6H_4(CH_3)_2 + HCl$

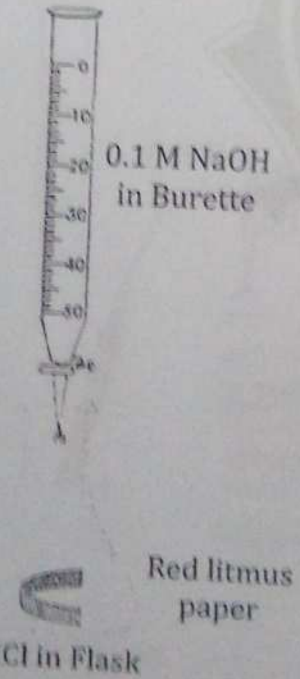
$C_6H_6 + n\ CH_3Cl \rightarrow C_6H_{6-n}(CH_3)_n + HCl$

Requirements of titration reaction

1. Single = no side reactions
2. Rapid
3. Stoichiometric
4. Complete at the EP
5. Feasible (standard solution, indicator, measuring instruments)

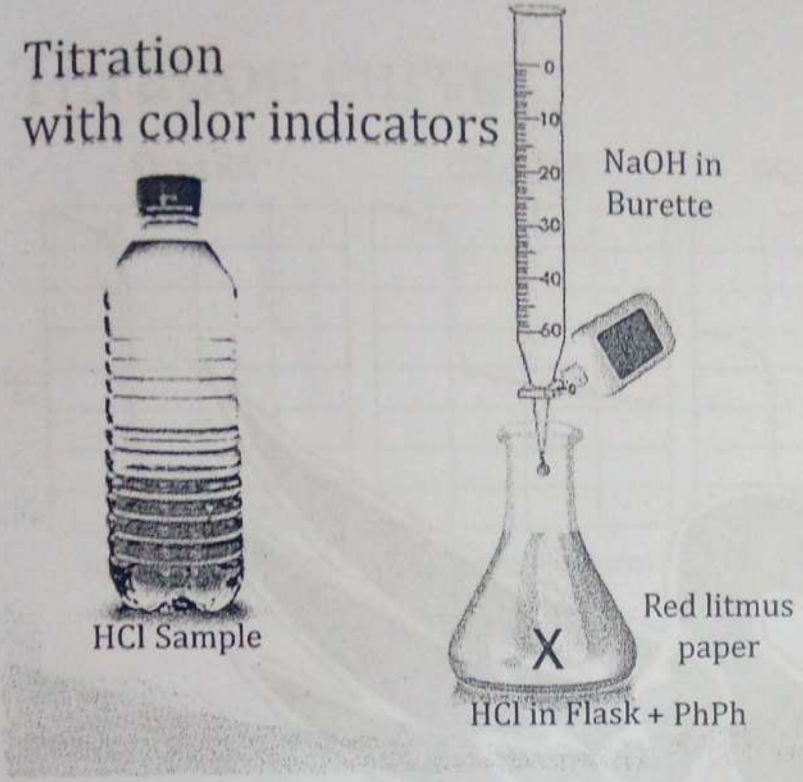
Titration with litmus paper

HCl Sample



Titration
Sample
Titrant
Indicator
    litmus paper
    color indicator
    pH-meter

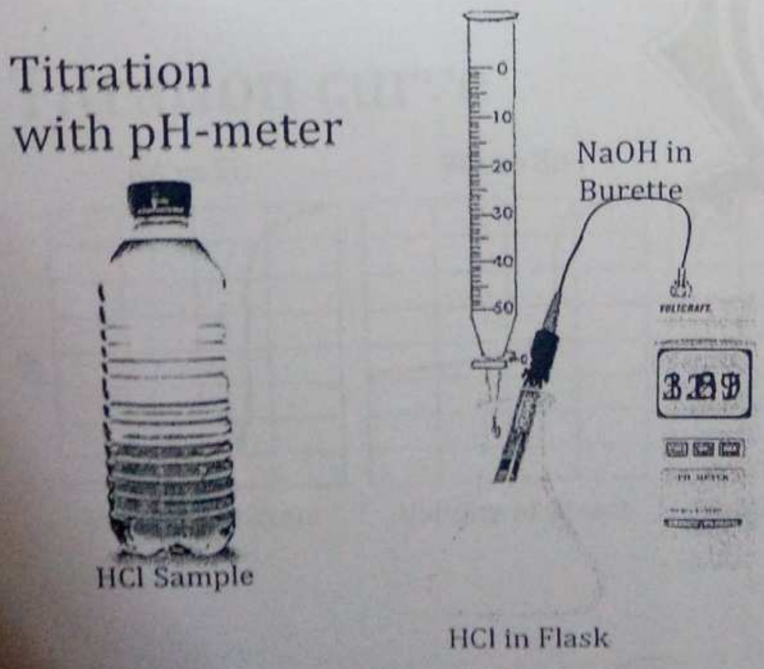
Titration
with color indicators

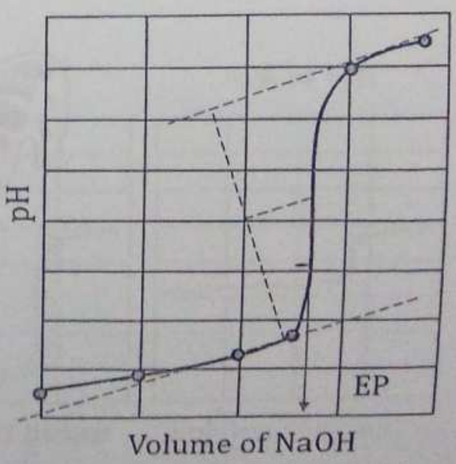


Phenolphthalein
Acidic medium: colorless
Basic medium: pink

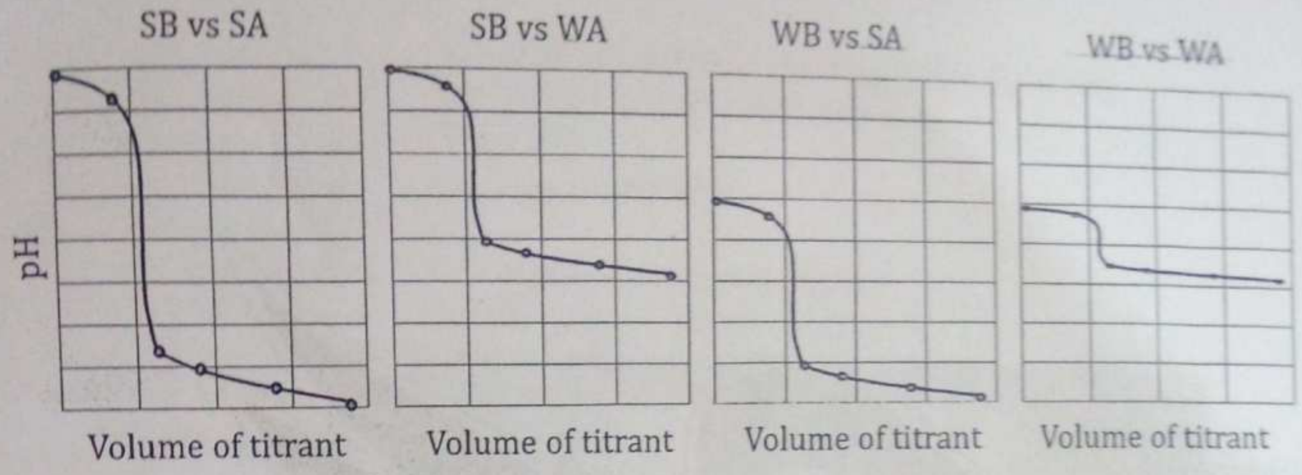
At End Point:
PhPh turns pink

Titration
with pH-meter

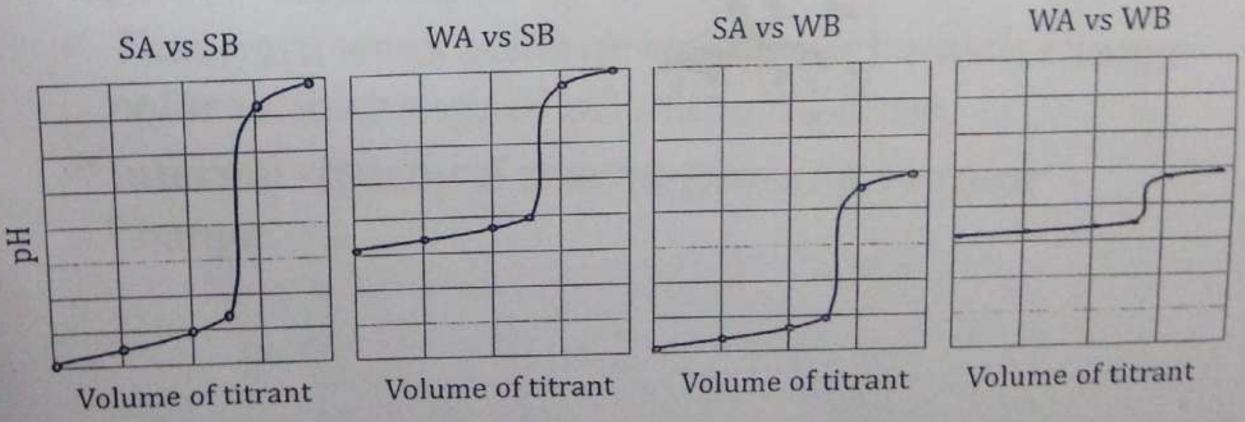




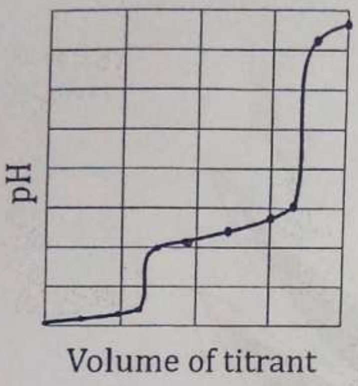
Titration curve



Titration curve



Titration curve



1. A mixture of two acids (e.g. HCl/CH_3COOH)
the difference in pKa should be ≥ 4
EP_{HCl}=EP1
EP_{CH_3COOH} = EP2-EP1

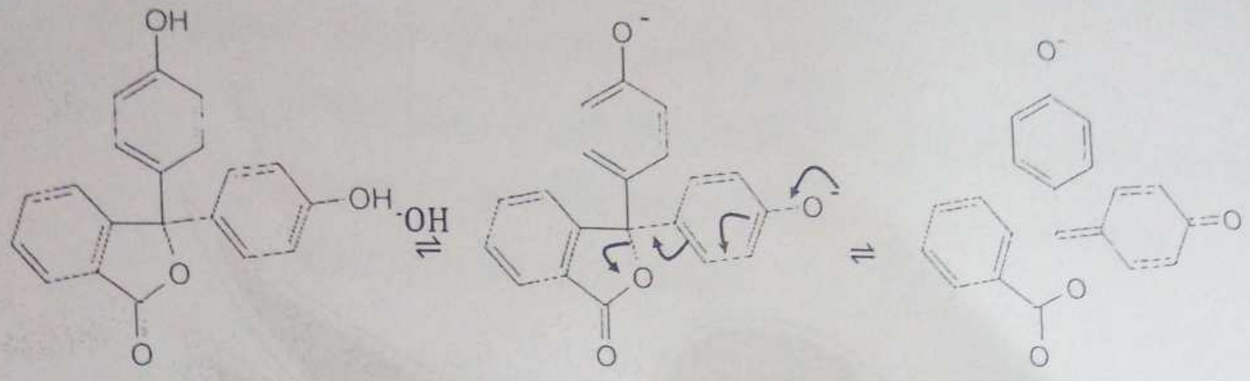
2. A diprotic acids (e.g. H_2SO_4)
the difference in pKa should be ≥ 4

Diprotic acid	K_1	K_2	K_1/K_2
Succnic acid	6.4×10^{-5}	2.7×10^{-6}	24
Oxalic acid	5.9×10^{-2}	6.4×10^{-5}	920
Maleic acid	1.2×10^{-2}	3.0×10^{-7}	4×10^{4}

Color Indicators

- ✓ These are weak acids or weak bases which change color with change of pH of the medium.
- ✓ internal structural rearrangements → color change

Color Indicators



Phenolphthalein

Color Indicators

- ✓ These are weak acids or weak bases which change color with change of pH of the medium.
- ✓ internal structural rearrangements → color change
- ✓ Change color over a range of 2 pH units

  Acidic: $pH = PK_{ind} \pm 1$

  Basic: $pOH = PK_{ind} \pm 1$

Color Indicators

✓ Choose the right indicator:

1. from the TC, determine the pH range of the EP
2. choose an indicator whose color changes within the EP pH range

Color Indicators

✓ Methyl orange:

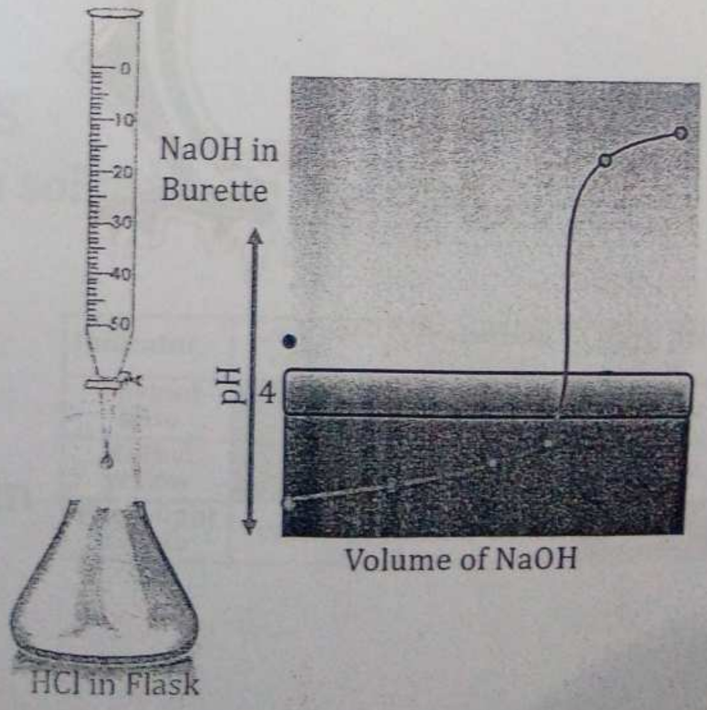
If 0.01 M HCl,

pH=2 (orange red)

If 0.01 M HCN (pKa 9.21),

pH= 5.61 (yellow)

Transition range: 3.1-4.4



Color Indicators

Indicator	Low pH color	Transition pH range	High pH color
Thymol blue	red	1.2–2.8	yellow
Methyl yellow	red	2.9–4.0	yellow
Methyl orange	red	3.1–4.4	yellow
Methyl red	red	4.4–6.2	yellow
Phenol red	yellow	6.4–8.0	red
Phenolphthalein	colorless	8.3–10.0	pink
Alizarine Yellow R	yellow	10.2–12.0	red

Color Indicators

✓ What is the color of a solution of CH_3COOH pH= 5 in:

a. Thymol blue

b. Methyl yellow

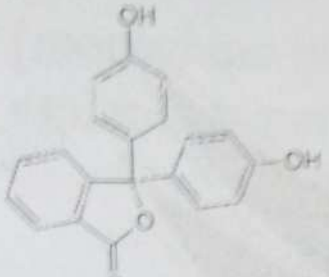
c. phenolphthalein

Indicator	Low pH color	Transition pH range	High pH color
Thymol blue	red	1.2–2.8	yellow
Methyl yellow	red	2.9–4.0	yellow
Phenolphthalein	colorless	8.3–10.0	pink

Color Indicators

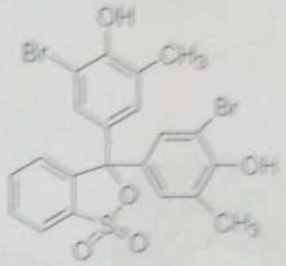
✓ Chemical Groups of Acid-Base Indicators:

Phthalein indicators



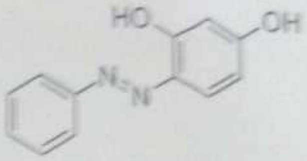
Phenolphthalein

Sulphonephthalein indicators



Bromocresol purple

Azo indicators



2,4-Dihydroxyazobenzene

Color Indicators

✓ Problems associated with acid-base indicators:

1. wide pH-range

Use mixed indicators: a mixture of thymol blue and cresol red (6 : 1 parts)it is violet at pH 8.4, blue at 8.3 and rose at 8.2.

Color Indicators

✓ Problems associated with acid-base indicators:

2. blunt color change

Use screened Indicator: organic dye+Indicator e.g. (methylene blue/methyl orange) color changes from violet to green instead of orange to yellow.

Color Indicators

✓ Problems associated with acid-base indicators:

3. not suitable for all types of titration

Use universal (multirange) indicator

phenolphthalein
methyl red
bromothymol blue
thymol blue

pH range	Description	Colour
<3	Strong acid	Red
3-6	Acid	Yellow
7	Neutral	Green
8-11	Alkaline	Blue
> 11	Strong alkaline	violet

titrant NaOH or strong base we use Ph Ph
" " HCl " acid " " methyl orange

Types of acid-base titrations

1. Direct Acid-Base Titration

Sample: acid or base

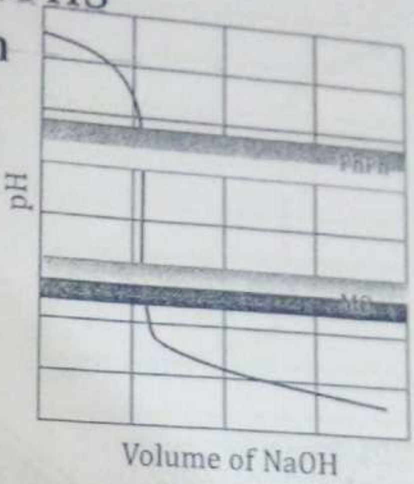
Titrant: base or acid

Indicator: acid-base indicator

Example: **Sample**: KOH

Titrant: Standard HCl

Indicator: MO or PhPh



calculations

$HCl + NaOH \rightarrow NaCl + H_2O$

moles of sample = # moles of titrant

$C_{sample} \cdot V_{sample} = C_{titrant} \cdot V_{titrant}$

$H_2SO_4 + 2\,NaOH \rightarrow Na_2SO_4 + 2H_2O$

$\frac{\#\text{moles of } H_2SO_4}{\#\text{moles of } NaOH} = \frac{1}{2}$

Types of acid-base titrations

2. substitution titration

Sample: salt of weaker acid or of weaker base

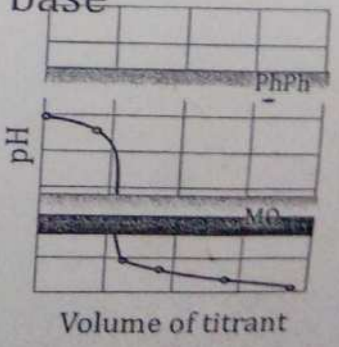
Titrant: stronger acid or stronger base

Indicator: acid-base indicator

Example: **Sample**: CH_3COONa

Titrant: Standard HCl

Indicator: MO



Types of acid-base titrations

3. residual or back titration

Sample: acid or base

Standard: known Xss of St base or acid

Titrant: standard acid or base

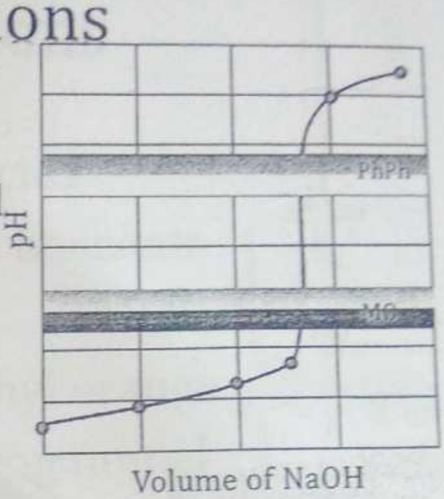
Indicator: acid-base indicator

Example: **Sample**: NH_3

Standard: known xss HCl

Titrant: Standard KOH

Indicator: MO or PhPh



Types of acid-base titrations

3. residual or back titration

Reasons of residual or back titration

1. **Volatile substances** e.g. NH_3
2. **Insoluble** e.g. ZnO
3. **Requires heating** e.g. esters
4. **Requires excess** e.g. lactic acid

Types of acid-base titrations

4. Biphasic titration

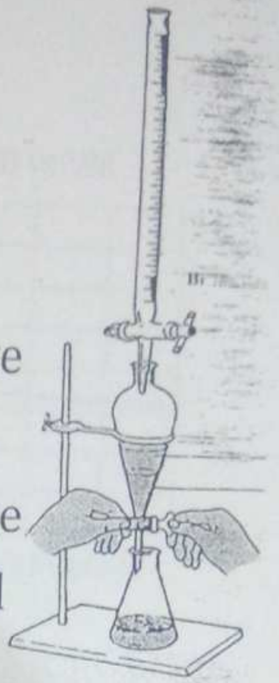
Sample: salts of insoluble aromatic acids

e.g. sodium salicylate or sodium benzoate

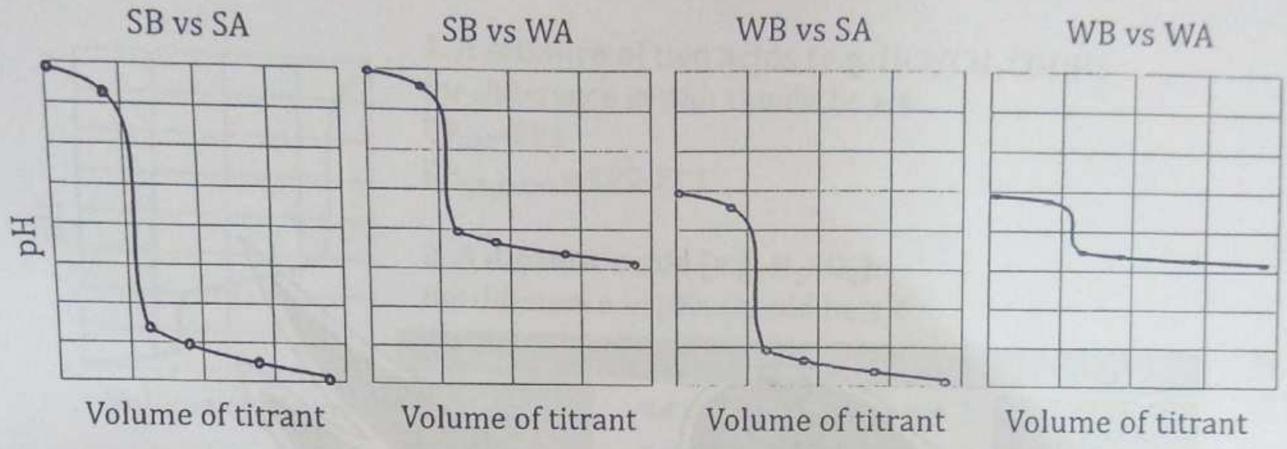
Titrant: HCl

Indicator: bromophenol blue or methyl orange

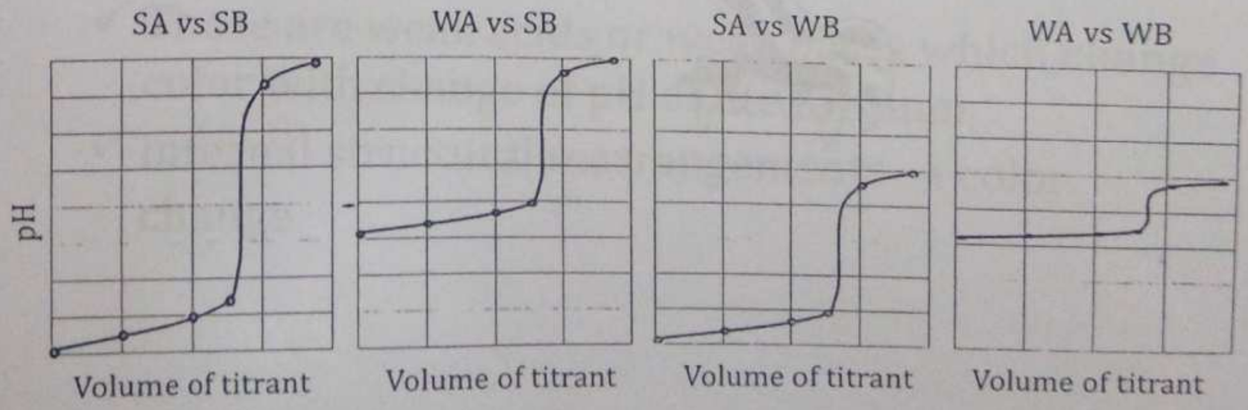
Solvent: water and ether in a separating funnel



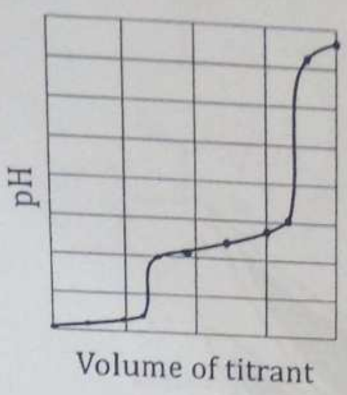
Titration curve


SB vs SA
SB vs WA
WB vs SA
WB vs WA

Titration curve


SA vs SB
WA vs SB
SA vs WB
WA vs WB

Titration curve



1. A mixture of two acids (e.g. HCl/CH_3COOH)
the difference in pKa should be ≥ 4
$EP_{HCl}=EP1$
$EP_{CH_3COOH} = EP2\text{-}EP1$

2. A diprotic acids (e.g. H_2SO_4)
the difference in pKa should be ≥ 4

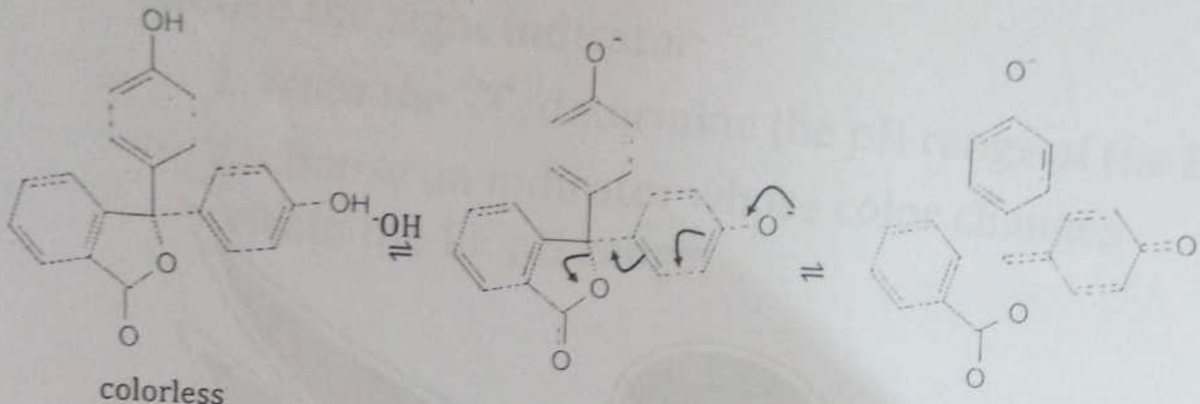
Diprotic acid	K_1	K_2	K_1/K_2
Succnic acid	6.4×10^{-5}	2.7×10^{-6}	24
Oxalic acid	5.9×10^{-2}	6.4×10^{-5}	920
Maleic acid	1.2×10^{-2}	3.0×10^{-7}	4×10^4

$\frac{K_1}{K_2}$ على الأقل 10^4

Color Indicators

- ✓ These are weak acids or weak bases which change color with change of pH of the medium.
- ✓ internal structural rearrangements → color change

Color Indicators



Phenolphthalein

Color Indicators

- ✓ These are weak acids or weak bases which change color with change of pH of the medium.
- ✓ internal structural rearrangements → color change
- ✓ Change color over a range of 2 pH units

  Acidic: $pH = PK_{ind} \pm 1$

  Basic: $pOH = PK_{ind} \pm 1$

Color Indicators

- ✓ Choose the right indicator:
  1. from the TC, determine the pH range of the EP
  2. choose an indicator whose color changes within the EP pH range

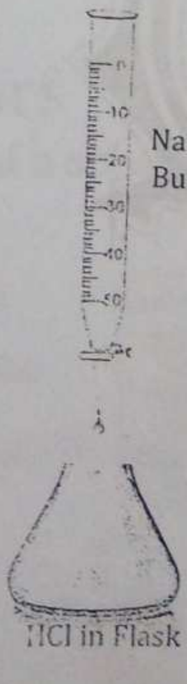
Color Indicators

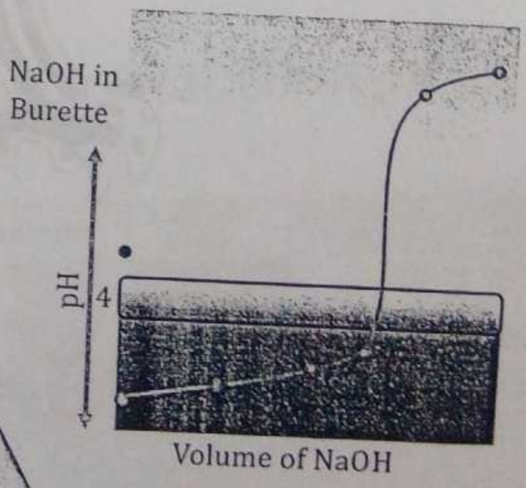
✓ Methyl orange:

If 0.01 M HCl,
pH=2 (orange red)

If 0.01 M HCN (pKa 9.21),
pH= 5.61 (yellow)

Transition range: 3.1-4.4





Color Indicators

Indicator	Low pH color	Transition pH range	High pH color
Thymol blue	red	1.2–2.8	yellow
Methyl yellow	red	2.9–4.0	yellow
✓ Methyl orange	red	3.1–4.4	yellow
Methyl red	red	4.4–6.2	yellow
Phenol red	yellow	6.4–8.0	red
✓ Phenolphthalein	colorless	8.3–10.0	pink
Alizarine Yellow R	yellow	10.2–12.0	red

Color Indicators

✓ What is the color of a solution of CH_3COOH pH= 5 in:

a. Thymol blue

b. Methyl yellow

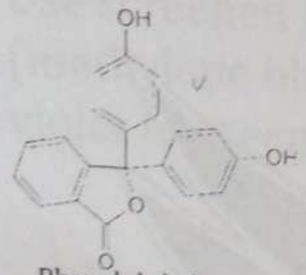
c. phenolphthalein

Indicator	Low pH color	Transition pH range	High pH color
Thymol blue	red	1.2–2.8	yellow
Methyl yellow	red	2.9–4.0	yellow
Phenolphthalein	colorless	8.3–10.0	pink

Color Indicators

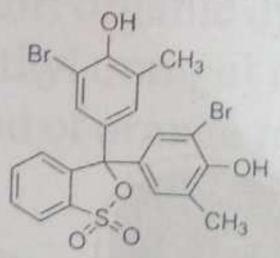
✓ Chemical Groups of Acid-Base Indicators:

Phthalein indicators



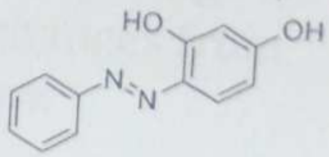
Phenolphthalein

Sulphonephthalein indicators



Bromocresol purple

Azo indicators



2,4-Dihydroxyazobenzene

Color Indicators

✓ Problems associated with acid-base indicators:

1. wide pH-range

Use mixed indicators: a mixture of thymol blue and cresol red (6 : 1 parts)it is violet at pH 8.4, blue at 8.3 and rose at 8.2.

Color Indicators

✓ Problems associated with acid-base indicators:

2. blunt color change

Use screened Indicator: organic dye+Indicator e.g. (methylene blue/methyl orange) color changes from violet to green instead of orange to yellow.

Color Indicators

✓ Problems associated with acid-base indicators:

3. not suitable for all types of titration

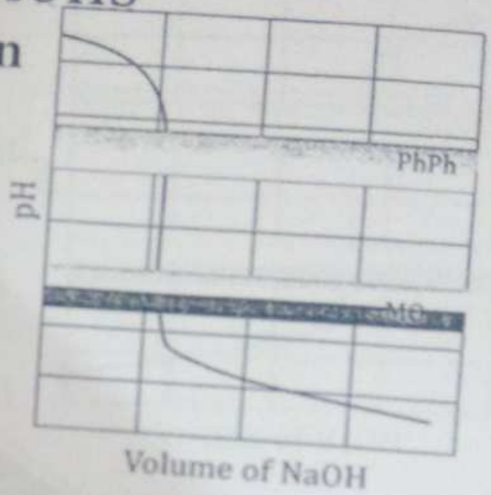
Use universal (multirange) indicator

phenolphthalein
methyl red
bromothymol blue
thymol blue

pH range	Description	Colour
<3	Strong acid	Red
3-6	Acid	Yellow
7	Neutral	Green
8-11	Alkaline	Blue
> 11	Strong alkaline	Violet

Types of acid-base titrations

1. Direct Acid-Base Titration



Sample: acid or base

Titrant: base or acid

Indicator: acid-base indicator

Example: **Sample**: KOH
Titrant: Standard HCl
Indicator: MO or PhPh

Types of acid-base titrations

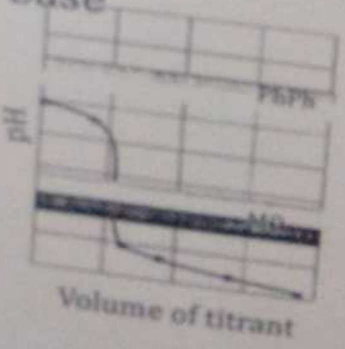
2. substitution titration

Sample: salt of weaker acid or of weaker base

Titrant: stronger acid or stronger base

Indicator: acid-base indicator

Example: **Sample**: CH_3COONa
Titrant: Standard HCl
Indicator: MO



Types of acid-base titrations

3. residual or back titration

Sample: acid or base

Standard: known Xss of St base or acid

Titrant: standard acid or base

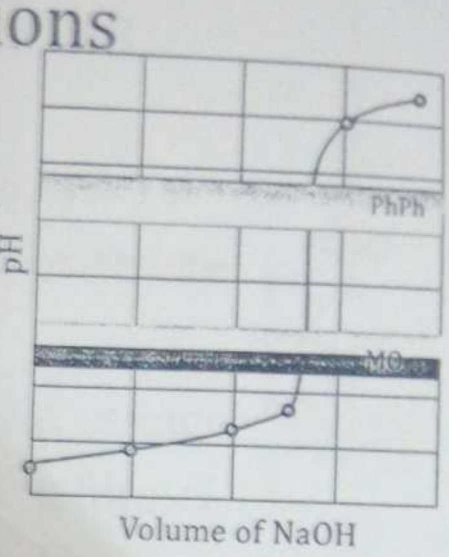
Indicator: acid-base indicator

Example: **Sample**: NH_3

Standard: known xss HCl

Titrant: Standard KOH

Indicator: MO or PhPh



Types of acid-base titrations

3. residual or back titration

Reasons of residual or back titration

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2. **Insoluble** e.g. ZnO
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4. **Requires excess** e.g. lactic acid

Types of acid-base titrations

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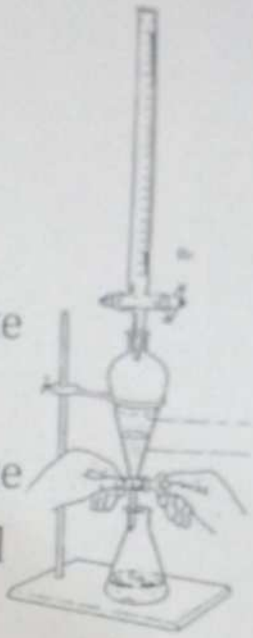
Sample: salts of insoluble aromatic acids

e.g. sodium salicylate or sodium benzoate

Titrant: HCl

Indicator: bromophenol blue or methyl orange

Solvent: water and ether in a separating funnel



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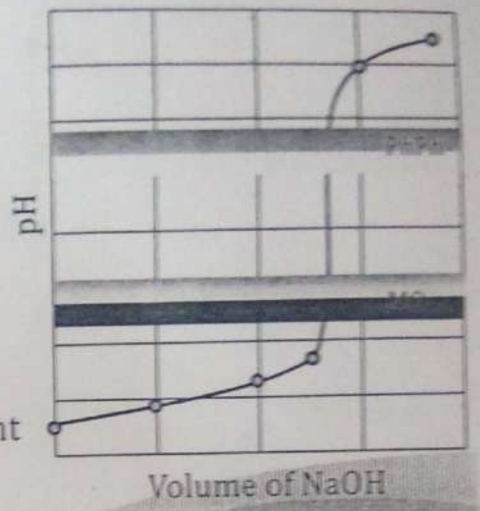
Applications of acid-base titration



1. Determination of HNO_3

Sample: HNO_3

Type: Direct acid-base titration

Titrant: 0.1 M NaOH

Indicator: PhPh (colorless to pink)
MO (orange to yellow)

Calculations:

# of moles of sample = # of moles of titrant

$C_{sample}.V_{sample} = C_{titrant}.V_{titrant}$

$C_{sample} = (C_{titrant}.V_{titrant})/V_{sample}$

$= (0.1\ M \times EP\ mL)/10\ mL$

Applications of acid-base titration

2. Determination of NH_3

Sample: NH_3

Type: back acid-base titration

Standard: Known excess HCl

Titrant: 0.1 M Na_2CO_3

Indicator: MO (orange to yellow)

Applications of acid-base titration

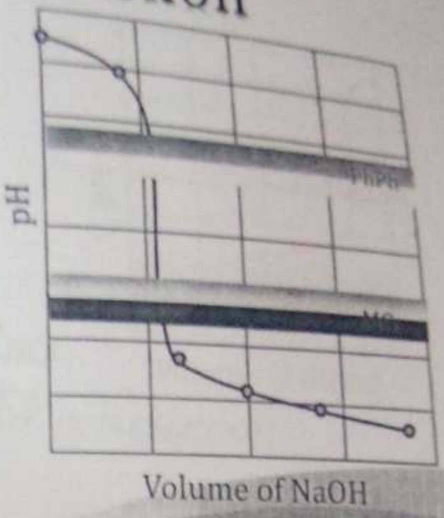
3. **Determination of CsOH**

Sample: CsOH

Type: direct acid-base titration

Titrant: St. HCl

Indicator: PhPh (pink to colorless)
MO (yellow to orange)



Applications of acid-base titration

4. **Determination of H_3BO_3**

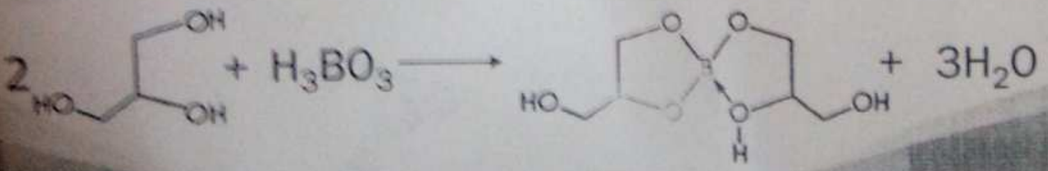
Sample: H_3BO_3 (a very weak acid; pKa=9.23)

Acid enhancer: glycerol

Type: direct acid-base titration

Titrant: 0.1 M NaOH

Indicator: PhPh (colorless to pink)



Applications of acid-base titration

3. Determination of CsOH

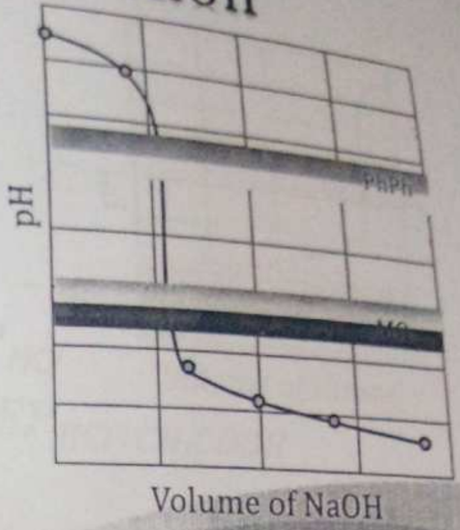
Sample: CsOH

Type: direct acid-base titration

Titrant: St. HCl

Indicator: PhPh (pink to colorless)

MO (yellow to orange)



Applications of acid-base titration

4. Determination of H_3BO_3

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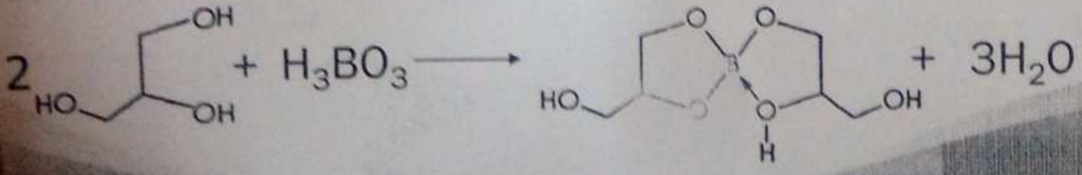
Acid enhancer: glycerol

Type: direct acid-base titration

Titrant: 0.1 M NaOH

Indicator: PhPh (colorless to pink)



Applications of acid-base titration

5. Determination of HCl/CH$_3$COOH

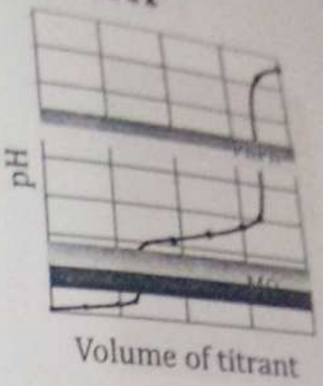
Sample: HCl/CH$_3$COOH

Type: Direct acid-base titration

Titrant: 0.1 M NaOH

Indicator: MO (orange to yellow)→EP_{HCl}

PhPh (colorless to pink) →EP_{HCl+CH_3COOH}



Applications of acid-base titration

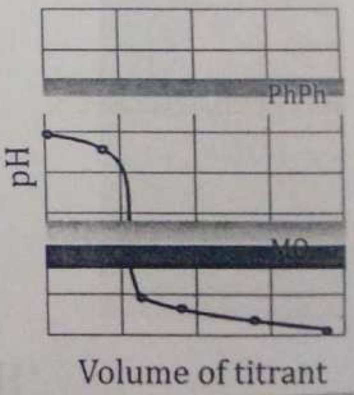
6. Determination of NaCN

Sample: NaCN

Type: replacement acid-base titration

Titrant: 0.1 M HCl

Indicator: MO (orange to yellow)



Applications of acid-base titration

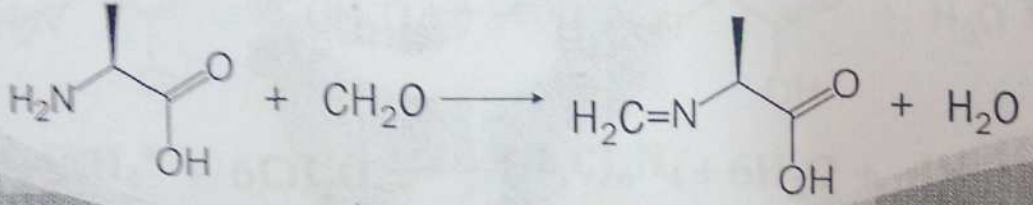
7. Determination of amino acids

Sample: amino acid (glycine or alanine)

Type: Formol titration (addition of HCHO)

Titrant: 0.1 M NaOH

Indicator: PhPh (colorless to pink)



Applications of acid-base titration

8. Determination of ammonium salts

Sample: ammonium salt

Type: Formol titration (addition of HCHO)

Titrant: 0.1 M NaOH

Indicator: PhPh (colorless to pink)

$$4NH_4^+ + 6CH_2O \longrightarrow (H_2C)_6N_4 + 6H_2O + 4H^+$$

Applications of acid-base titration

Kjeldahl method

Sample: organic nitrogenous compounds

Procedures:

1. Degradation, 2. Replacement and reflux, 3. Back titration

In the digestion step,

- Na_2SO_4 to increase boiling point of H_2SO_4
- a catalyst (Hg/Se/Cu) is added to hasten the reaction

Disadvantages: time-consuming

not for cyano, azo or nito cpds

dangerous (Δ/H_2SO_4)

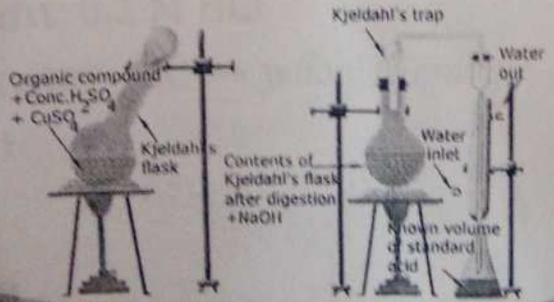
Applications of acid-base titration

Kjeldahl method

Sample: organic nitrogenous compounds

Procedures:

1. Degradation, 2. Replacement and reflux, 3. Back titration


Kjeldahl's trap
Water out
Organic compound + Conc.H_2SO_4 + $CuSO_4$
Kjeldahl's flask
Contents of Kjeldahl's flask after digestion +NaOH
Water inlet
Known volume of standard acid

Applications of acid-base titration

Kjeldahl method

Sample: organic nitrogenous compounds

Procedures:

1. Degradation, 2. Replacement and reflux, 3. Back titration

In the digestion step,

Na_2SO_4 to increase boiling point of H_2SO_4

a catalyst (Hg/Se/Cu) is added to hasten the reaction

Disadvantages: time-consuming

not for cyano, azo or nito cpds

dangerous (Δ/H_2SO_4)

Applications of acid-base titration

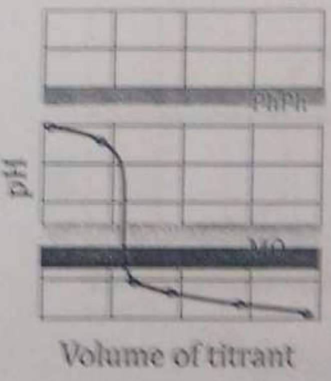
10. Determination of $NaHCO_3$

Sample: $NaHCO_3$

Type: replacement acid-base titration

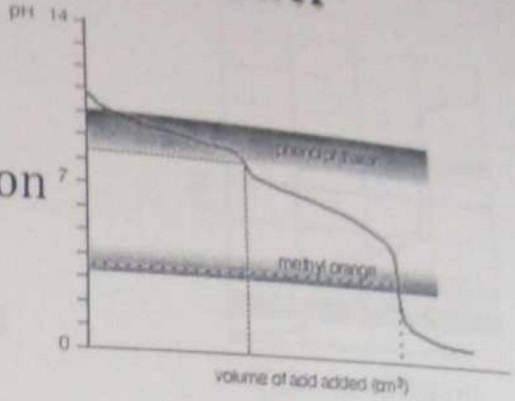
Titrant: 0.1 M HCl

Indicator: MO → *yellow to orange*



Applications of acid-base titration

11. Determination of Na_2CO_3



Sample: Na_2CO_3

Type: replacement acid-base titration

Titrant: 0.1 M HCl

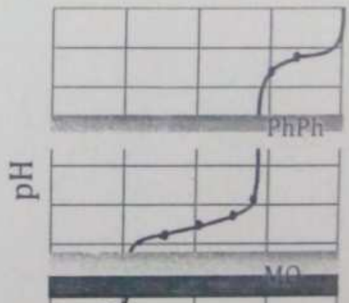
Indicator: PhPh $\rightarrow EP_1 = \frac{1}{2} EP_{Na_2CO_3}$

MO $\rightarrow EP_2 = EP_{Na_2CO_3}$

$EP_1 = \frac{1}{2} EP_2$

Applications of acid-base titration

12. Determination of H_3PO_4



Sample: H_3PO_4

Type: direct acid-base titration

Titrant: 0.1 M NaOH

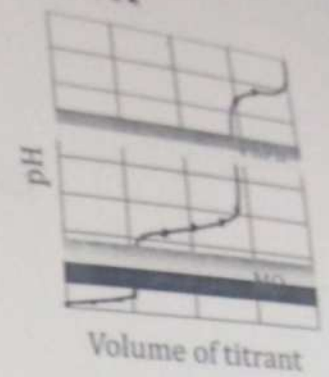
$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ $pK_1 = 2.12$

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$ $pK_2 = 7.21$

$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$ $pK_3 = 12.3$

Applications of acid-base titration

12. Determination of H_3PO_4



Sample: H_3PO_4

Type: direct acid-base titration

Titrant: 0.1 M NaOH

Indicator: MO→$\mathcal{EP}_1 = \frac{1}{3} EP_{H_3PO_4}$

PhPh→$\mathcal{EP}_2 = \frac{2}{3} EP_{H_3PO_4}$

For EP_3:

$2H_3PO_4 + 3CaCl_2 \rightleftharpoons Ca_3(PO_4)_2 + 6HCl$

Applications of acid-base titration

14. Determination of H_3PO_4/HCl

Sample: H_3PO_4/HCl

Type: Direct acid-base titration

Titrant: 0.1 M NaOH

Indicator: MO →$EP_{HCl} + \frac{1}{3} EP_{H_3PO_4}$

PhPh → $EP_{HCl} + \frac{2}{3} EP_{H_3PO_4}$

Applications of acid-base titration

15. Determination of $NaOH/Na_2CO_3$

Sample: $NaOH/Na_2CO_3$

Type: Direct/replacement acid-base titration

Titrant: 0.1 M HCl

Indicator: PhPh $\rightarrow EP_{NaOH} + \frac{1}{2}EP_{Na_2CO_3}$

MO $\rightarrow EP_{NaOH} + EP_{Na_2CO_3}$

Applications of acid-base titration

16. Determination of $Na_2CO_3/NaHCO_3$

Sample: $Na_2CO_3/NaHCO_3$

Type: replacement acid-base titration

Titrant: 0.1 M HCl

Indicator: PhPh $\rightarrow \frac{1}{2}EP_{Na_2CO_3}$

MO $\rightarrow EP_{Na_2CO_3} + EP_{NaHCO_3}$

Applications of acid base titration

17. Determination of HCl/ H_3BO_3

Sample: HCl/ H_3BO_3

Type: Direct acid-base titration

Titrant: standard NaOH

Indicator: before glycerol → EP_{HCl}

After glycerol → $EP_{HCl} + EP_{H_3BO_3}$

Limitations of aq. acid-base titration

1. Not suitable for very weak acids or bases

e.g. phenol (pKa=10), aniline (pKb=9.4)

2. Cannot differentiate between strong acids

$HClO_4$ and HNO_3

2. Not suitable for insoluble Acids or bases

e.g aniline & fatty acids

4. Not suitable for the titration of weak acid vs weak bases

5. Not suitable for salts of strong acids/strong bases